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Topics for Teaching: Chemistry in Nature

Changing Colours of Autumn

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Abstract: Changes in the dominant pigments in leaves of deciduous trees lead to beautiful autumnal hues. However, physiological and ecological reasons for the colours are still open for debate.

Keywords: Chemical education · Leaves · Photosynthesis · Pigments

> *"That time of year thou mayst in me behold*
> *When yellow leaves, or none, or few, do hang*
> *Upon those boughs which shake against the cold."*[1]

Nature has engineered the green pigments chlorophylls *a* and *b* in leaves to optimise light-harvesting and energy conversion in photosynthesis. Chlorophylls *a* and *b* are porphyrinato coordination compounds containing Mg^{2+} coordinated within a square-planar arrangement of nitrogen-donor atoms. Fig. 1a displays the structures of chlorophylls *a* and *b*, and the conjugation in the ring system results in light absorption in the visible region. Chlorophyll *a* has absorption maxima at 662 and 430 nm (red and blue-violet light, respectively), while chlorophyll *b* exhibits absorption maxima at 642 and 453 nm. (The difference between absorbed and reflected light was described in a previous Education Column in this series.[2]) Light absorption by chlorophylls initiates a series of reactions involving the metalloenzyme photosystem II (PSII) which converts H_2O to O_2 (Eqn. (1)).

$$2H_2O \xrightarrow{h\nu,\ \{Mn_4CaO_5\}} O_2 + 4H^+ + 4e^- \tag{1}$$

The structure and function of PSII is complex[3,4] and we focus only on the oxygen-evolving complex (OEC) at which the four-electron oxidation process in Eqn. (1) occurs. This is facilitated by one-electron changes in the oxidation states of the Mn centres in an Mn_4CaO_5 cluster (Fig. 1b). Fig. 1c illustrates the Kok cycle that describes how the OEC catalyses reaction 1.[4]

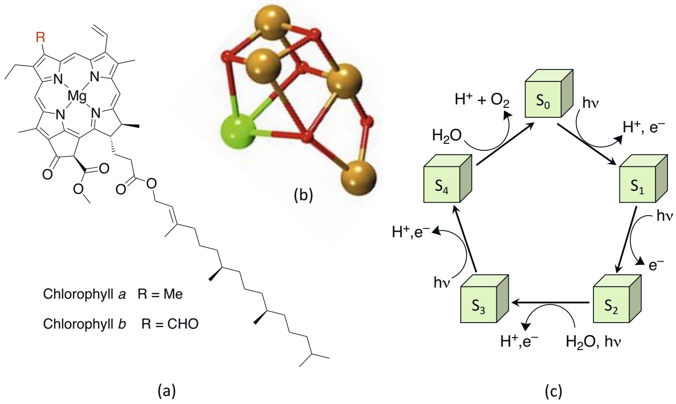

Fig. 1. (a) Structures of chlorophylls *a* and *b*. (b) The structure[3] of the cubane-like Mn_4CaO_5 active site in the OEC in PSII (datacode 4UB6 retrieved from the Protein Data Bank https://www.rcsb.org). Colour code: Mn brown; O red; Ca green. (c) The Kok cycle in photosystem II; S_0, S_1, S_2, S_3 and S_4 denote the Mn_4-unit in different oxidation states; S_4 is a transient state and S_1 is the dark state.

Two questions now arise. Firstly, how does photosynthesis occur in plants where the leaves are not green, *e.g.* species of *Acer* with all-year-round red leaves (Fig. 2a)? Second, how and why do leaves change their colour in the autumn (Fig. 2b, 2c)?

In plants and trees that possess red leaves throughout the year, the green colour arising from chlorophylls is masked by red pigments, mainly *anthocyanins* but also *betalains*, some *carotenoids* (see later), *thiarubrine A*, some *terpenoids*, and *3-deoxyanthocyanins*.[5] The dominant anthocyanin pigment is cyanidin-3-*O*-glucoside (Fig. 3a), which is also present in various edible fruits such as plums, peaches, blackcurrants and blood oranges. Interestingly, there are metabolic disadvantages associated with the presence of anthocyanins in red-leaved flora: seven or more enzymes are involved in the biosynthesis of cyanidin, and there is a metabolic price to pay for the covalent connection of the cyanidin and monosaccharide units in cyanidin-3-*O*-glucoside.[5] The roles of anthocyanins have been, and still are, a matter for debate. In the late 1800s, it was observed that the production of anthocyanins increased when a plant was exposed to low temperatures and high light conditions. In the mid-1900s, scientists noted that ultraviolet (UV) light stimulated anthocyanin production, suggesting that anthocyanins protect the plant from UV damage. However, anthocyanins do not absorb strongly in the region (285–320 nm, UV-B radiation) which causes most damage to plant cells.[6] Anthocyanins can play multiple roles in plants, including photoprotection and photoinhibition. One interesting role as a photoinhibitor is in acting as a CO_2 sink,[8] with sugars produced by photosynthesis being trapped in the anthocyanin structure (Fig. 3a). Anthocyanins also moderate photooxidative damage in leaves by scavenging free radicals and other reactive oxygen species (ROS), although aspects of this are still questioned.[5,7] The red colouration may act as a plant defence by discouraging herbivorous insects.[8,9] Gould summarised the miscellaneous roles by saying that anthocyanins "are the Swiss army knife of the plant kingdom".[5]

We turn now to the question of the changing colours of autumn leaves, focusing first on the chemical perspective. Optimal conditions for the biosynthesis of chlorophyll are warm weather and sunlight. Plants produce less chlorophyll as temperatures decrease and daylight hours shorten from summer to autumn. In addition, existing chlorophyll gradually degrades. Both green and red leaves also contain yellow and orange carotenoid pig-

Fig. 2. (a) Leaves of some species of *Acer* remain red throughout the year. Cherry tree orchard in Canton Solothurn changing colour from (b) green in spring and summer to (c) yellow-orange in autumn. (d) Some dead leaves of the European beech (*Fagus sylvatica*) are retained through the winter. Photo credits: Catherine Housecroft (a)–(c); Edwin Constable (d).

ments. *Carotenoids* comprise *carotenes* and *xanthophylls*, and are polyenes. The extended π-system leads to absorption maxima in the visible region. Carotenes (*e.g.* β-carotene, Fig. 3b) are hydrocarbons. Xanthophylls (*e.g.* lutein, Fig. 3c) are derivatives of carotenes containing OH or related substituents. In its solution absorption spectra, β-carotene exhibits absorption maxima around 450 and 479 nm (absorbs blue-violet light) and the maxima for solutions of lutein are similar.

Autumn leaf colour changes usually occur within a few weeks before leaf-fall, although some trees such as beech (species of *Fagus*) retain some of their dead leaves through the winter (Fig. 2d); this behaviour is known as *marcescence*. Yellow and orange leaf colouration results from the dominance of carotene and xanthophyll pigments as chorophylls degrade in autumn. In leaves that turn red in the autumn, two mechanisms are at work: the degradation of chlorophyll which exposes the colours of carotenes and xanthophylls, and the biosynthesis of anthocyanins. A change to brown results from the degradation of chlorophyll, carotene and xanthophyll pigments.[7,8] While the chemistry of the pigments is understood, the physiological and ecological reasons behind the colour changes are far less defined. A key function underlying the colour changes to yellow, orange and red is the need for a deciduous tree to store nitrogen typically as amino acids after photosynthesis stops for the winter.[8] In an instructive recent review,[8] Lev-Yadun considers the "hypotheses, agreements and disagreements" in the quest to understand autumnal colour changes.

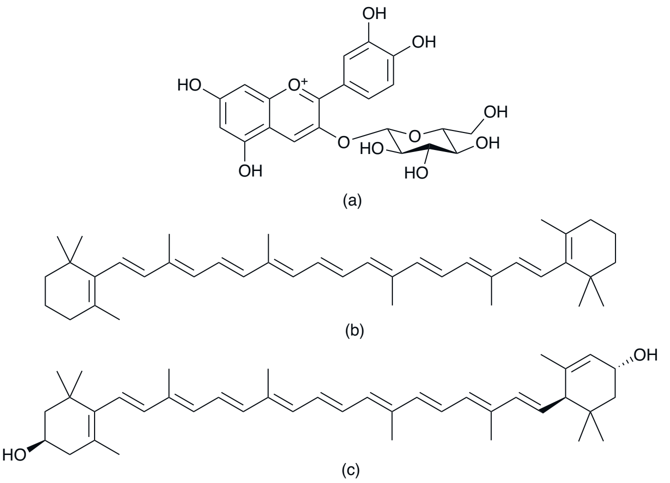

Fig. 3. The structures of (a) cyanidin-3-*O*-glucoside, (b) β-carotene, and (c) lutein.

Finally, a comment on evergreen trees. Typically, trees that remain green throughout the winter possess needles (*e.g. Pinus sp., Picea sp.*); exceptions include holly (*Ilex sp.*) and ivy (*Hedera sp.*). Unlike deciduous trees that tend to live in temperate climates, evergreen trees tend to be found in cold climates, at high altitudes, and/or in nutrient-poor soils, and their green needles have evolved to cope with low temperatures. Photosynthesis in evergreen trees does not necessarily continue throughout the whole winter. When temperatures drop below *ca.* –5 °C, photosynthesis ceases but can restart when temperatures rise again.

This article examined the pigments in green, yellow, orange, red, and brown leaves. Although the chemistry of the pigments is well established, physiological and ecological explanations for the colour changes remain open for further research.

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This column is one of a series designed to attract teachers to topics that link chemistry to Nature and stimulate students by seeing real-life applications of the subject.